

Novel Materials Synthesis at High Pressures and Temperatures¹

C.S. Yoo, H. Cynn, and M. Nicol*

Lawrence Livermore National Laboratory, Livermore, California 94551, USA

** University of California, Los Angeles, California 90095, USA*

I. Extended abstract

The microscopic understanding of novel materials with advanced, optimized properties requires knowledge at the molecular or atomistic level of their structure, phase stability, and electronic, optical, vibrational, and mechanical properties, all of which can be altered by application of high pressures and temperatures. Recent advances of high pressure and temperature technologies, thus, provide extended opportunities in materials research for discovery of new properties and phenomena, invention of new exotic materials, and modification of chemical bond and crystal structure for advanced and desirable properties.

Many novel materials composed of the first- and second-row elements like diamond and cubic-boron nitride exhibit covalently bonded three-dimensional network structures. The extended network structures in these hard materials contrast with the molecular forms of the same elements like N₂, which typically involve strong covalent intramolecular bonds and only weak van der Waals interactions between the molecules. The highly local nature of the electrons in these molecular covalent bonds minimizes their potential energy, makes the bonds extremely stable, and acts as a barrier to reactions leading to network structures.

In contrast, the network structure is ubiquitous at high pressures, as unsaturated chemical bonds become unstable at high pressures with respect to associative, cross-linking reactions forming denser, more saturated species.² This is because at high pressures the kinetic energy of electrons dominates and the intermolecular interaction of isolated molecules becomes mostly repulsive in nature. Therefore, the electrons localized in isolated molecules at low pressures should eventually delocalize at sufficiently high pressures. Thus, applying high pressure is an excellent way to increase chemical reactivity of many molecules with strong covalent bonds.

Pressure increases the chemical reactivity; yet, there may exist a high activation barrier preventing the

problem is high temperature, which can be obtained by ohmically heating a diamond-anvil cell to several hundred degrees or laser-heating it to a few thousand degrees. On the other hand, such an activation barrier also existing in the reverse process provides opportunities to quench new materials and metastable phases at ambient conditions.

Over the past few years, we have studied various chemical reactions at high pressures and temperatures,³ particularly among the first and second row elements with the emphasis on synthesis of superhard and energetic materials. In this paper, we describe the reactions of light elements such as boron and carbon with diatomic covalent molecules such as nitrogen and oxygen, yielding mostly hard materials.

Laser-heating technique was used to heat the sample and also initiate the reaction in a diamond-anvil cell. The reaction products were characterized by angle-resolved synchrotron x-ray diffraction⁴ and micro-Raman spectroscopy. Most of the elementary reactions described in this paper occur extremely rapidly and exothermically at high temperatures and pressures, similar to a laser combustion if not an explosion. These reactions yield various forms of technologically important nitrides and oxides, whose crystal structures strongly depend on the reaction pressure. For example, the boron-nitrogen reaction produces hexagonal-BN below approximately 10 GPa, but a cubic or wurzite form at higher pressures. The final products of these reactions at high pressures and temperatures are relatively well polycrystallized, with an exception in carbon-nitrogen reactions which typically result in an amorphous material. We also found a few new forms of nitrides and oxides at various P,T conditions, what appear to be metastable.

The exothermic nature of these elementary reactions seems to be common in many similar reactions forming various oxides, nitrides, and carbides, which characteristics could be used as a new synthetic route for novel super-hard materials as well as for new high explosives or propellants. Possible applications of these exothermic reactions in future will also be discussed.

References

- [1] C.S. Yoo and M.F. Nicol, *J. Phys. Chem.* **90**, 6726 (1986) and *ibid* **90**, 6732 (1986); A.I. Katz, D. Schiferl, and R.L. Mills, *J. Phys. Chem.* **88**, 3176 (1981).
- [2] C.S. Yoo, J. Akella, H. Cynn, M. Nicol, *Phys. Rev. B*, submitted (1997).
- [3] The synchrotron work was performed on the beamline 10-2 at the SSRL and x17c at the NSLS.

This work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under the contract number W-7405-ENG-48.